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MAR flow mapping of Analytical Chemistry Operations (Preliminary Report)

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INTRODUCTION

The recently released Supplemental Directive, NA-1 SD 1027, updates the radionuclide threshold values in DOE-STD-1027-92 CN1 to reflect the use of modern parameters for dose conversion factors and breathing rates. The directive also corrects several arithmetic errors within the original standard. The result is a roughly four-fold increase in the amount of weapons-grade nuclear material allowed within a designated radiological facility.

Radiological laboratory space within the recently constructed Radiological Laboratory Office and Utility Building (RLUOB) is slated to house selected analytical chemistry support activities in addition to small-scale actinide R&D activities. RLUOB is within the same facility operations envelope as TA-55. Consolidation of analytical chemistry activities to RLUOB and PF-4 offers operational efficiency improvements relative to the current pre-CMRR plans of dividing these activities between RLUOB, PF-4, and CMR.

RLUOB is considered a Radiological Facility under STD-1027 - "Facilities that do not meet or exceed Category 3 threshold criteria but still possess some amount of radioactive material may be considered Radiological Facilities." The supplemental directive essentially increases the allowable material-at-risk (MAR) within radiological facilities from 8.4 g to 38.6 g for ^{239}Pu. This increase in allowable MAR provides a unique opportunity to establish additional analytical chemistry support functions in RLUOB without negatively impacting either R&D activities or facility operations.

Individual radiological facilities are tasked to determine MAR limits (up to the Category 3 thresholds) appropriate to their operational conditions. This study presents parameters that impact establishing MAR limits for RLUOB and an assessment of how various analytical chemistry support functions could operate within the established MAR limits.

PARAMETERS

Parameters that impact facility MAR

Isotopes and mixtures

The release fractions used in generating the thresholds for Category 3 nuclear facilities are provided in a supplemental guidance document, NA-1 SD G 1027. These are intended to be conservative for a broad range of possible situations. If the facility has a final categorization of less than Hazard Category 3, it is a radiological facility such as RLUOB. Thus, Category 3 'thresholds' are essentially radiological facility 'limits'. The most commonly requested actinide analyses are for isotopes of plutonium, uranium, americium, thorium, and neptunium. Of these, only ^{239}Pu, ^{238}Pu, and ^{241}Am are

likely to be present in quantities that contribute significantly to MAR. NA-1 SD G 1027 presents the following values for maximum allowable MAR by isotope for radiological facilities.

Isotope (or Mat'l Type)	Activity (Ci)	Mass (g)
^{238}Pu	2.62	0.153
^{239}Pu	2.4	38.6
^{241}Am	2.89	0.842
^{235}U	14.6	6,760,000
^{237}Np	5.36	7,600
^{243}Am	2.89	14.5
MT-52		29 *
MT-83		0.18 *

Table 1. Hazard Category 3 radionuclide threshold quantities from Table 1 of "Revised Thresholds for Radionuclides" in NA-1 SD G 1027. Values for material types (*) are estimates based on nominal isotopic composition.

Physical form and containment

The revised Hazard Category 3 threshold quantities use revised dose conversion factors and a revised breathing rate. The final categorization is based on an unmitigated release of available hazardous material. For the purposes of hazard categorization, "unmitigated" is meant to consider material quantity, form, location, dispersibility and interaction with available energy sources. For our isotopes of interest, the limiting pathway for exposure has been identified as inhalation. Thus, the appropriate level of containment and ventilation is dependent upon the physical form of the material.

For most analytical chemistry analyses, material is in aqueous (acidic) solution after initial preparation. Sample handling and equipment venting occurs in either open-front hoods or gloveboxes, so both the chemical form and containment minimize potential for inhalation exposure. However, some analytical chemistry operations involve taking small samples to dryness on a hot plate or the combustion of larger quantities. Hazards associated with these operations are easily controlled by specific work authorization documents.

Types of operations

Analytical chemistry instrumental analyses usually generate very little waste, use low-hazard chemicals (primarily moderately strong acids), and use low-hazard instrumentation. Several preparation steps, however, involve small quantities of flammable solvents or high temperatures. Traditionally, these types of operations are routinely allowed within radiological facilities where quantities of materials are limited. Dissolution preparation steps may generate substantial quantities of Trans-Uranic (TRU) waste. Operating a radiological facility at higher MAR limits calls for careful process evaluation with special MAR limitations placed on specific operations or developing lower hazard alternatives.

Inventory control

Individual items with 0.5g of ^{239}Pu or higher are accountable material. RLUOB is not currently intended to handle accountable samples, and the administration of accountable material adds

considerable complexity and cost to facility operations. Occasionally, material transfers into RLUOB may contain an accountable amount of material in aggregate, but individual items are subaccountable.

MAR inventory procedures for a radiological facility may be more or less rigorous than for a nuclear facility, depending on the nuclide. The lower MAR limit mandates tracking of material to a much higher level of precision and accuracy to avoid exceeding the authorization basis. Rapid turnover of many small inventory items requires a responsive real-time database, but items may move within the facility envelope without formal time requirements for location updates. Samples for chemical analyses have, by definition, some uncertainty associated with their composition which may affect their MAR. However, they are reasonably well characterized before submission, so a very modest 'buffer' to the facility MAR limit should be sufficient to accommodate even gross errors in sample MAR - especially if samples are verified and corrected in a timely fashion.

Per "Radioactive Material Inventory Control at RC-1", PRO-C-DO-007, the radiological facility at TA-48 employs a 5% 'buffer' (i.e. MAR set at 95% of maximum as an administrative limit) under normal operating conditions. An additional 5% or so is 'reserved' to account for material in the ventilation system and for items that are not tracked in the MAR inventory (i.e. below 1/10,000 th of the facility MAR limit). As a new facility, RLUOB will not have any legacy or untracked items to account for, so will not need this additional 5% reserve. The tracking system used at TA-48 has worked well, and is a good starting point for future RLUOB operations.

MAR allocations

MAR allocations are purely administrative, since MAR at radiological facilities is reported at the facility level. They are, however, reasonable tools to ensure that certain activities do not jeopardize the ability of other processes to operate effectively. Examples of allocations include R&D activities, TRU and Low-Level (LL) waste storage, allowances for stock solutions and standards used in analyses, and reserved MAR for special-case samples or experiments. If reserves for special-case situations adversely impacts MAR allocations for routine activities, it is possible to obtain permission to temporarily exceed normal facility MAR limits to run special-case analyses.

Parameters that impact which analytical chemistry operations are established at RLUOB

Facility MAR limits

By far the most significant parameter is the total MAR made available for analytical chemistry operations. The supplemental directive essentially increases the allowable MAR within radiological facilities from 8.4 g to 38.6 g ^{239}Pu equivalents (PE) for the most common actinide nuclides.

RLUOB is currently designated a single radiological facility. However, RLUOB laboratory space is already physically separated into two major areas for secure (classified) operations and for open (unclassified) activities. Although there are no plans to do so, it is possible that each side (each set of laboratories) could be designated as a separate radiological facility with autonomous MAR operational limits. Alternatively, waste services and storage are contained in the basement, physically separated from active laboratory space. Although there are no plans to do so, it is feasible that the basement could be designated as a radiological facility with its own MAR operational limits. Dividing RLUOB into two or more separate radiological facilities would increase the overall MAR for operations while accomplishing many of the goals of MAR allocation.

Operational MAR

The primary parameter that impacts which specific analytical chemistry operations are suitable for RLUOB is the amount of radioactive material that is needed for running an analysis. This material, comprised of individual samples and any standards needed for analysis, is the *minimum* MAR associated with that analytical technique. For the purposes of this report, ^{239}Pu is reported to a minimum mass of 0.1 mg, while Am and ^{238}Pu are reported to a minimum of 0.01mg.

Most processes use very low amounts of material for the actual instrumental analyses, but start with high MAR and have successive preparation steps that reduce MAR while modifying the physical and chemical form of the sample. Thus, when determining which analyses are feasible for RLUOB, we also need to consider the requirements for sample preparation. In many cases, sample preparation can occur separated in time and location from sample analysis and be treated as semi-autonomous operations with independent MAR assignments.

To determine the MAR associated with each analytical chemistry operation, we have constructed flow maps that track the steps for each operation from original sample to final analysis. Steps in the flow map are defined by major changes in MAR. Steps also correspond to breaks in the process where samples could be packaged and transferred to another location. In most cases, these steps correspond to current practices, but for others, they correspond to reasonable changes that could be made if future preparation and analysis occur in separate facilities.

Figure 1 provides a very simplified map of most of the analytical chemistry operations of interest to weapons programs. This flow map includes basic preparation steps (oval boxes) such as dissolution and chemical separations. These preparation steps are tied to their associated analysis steps (rectangular boxes) by arrows. The MAR associated with a single 'average' sample and the amount of standards used in a single analysis are included in the step information box. Since many analyses involve dissolution of large solid samples, special attention is given to grouping steps that cascade from sample dissolutions (dashed boxes). Other steps initiate with splits from a solid or liquid sample.

The flow map segregates steps into major MAR columns that correlate with average MAR per sample and a corresponding number of samples that step can 'hold' at the new 38.6 g PE facility limit. Roughly, this segregation is "very high" for MAR over 1g of MT-52, "high" for MAR between 125 mg and 1 g, "moderate" for MAR between 25 mg and 125 mg, and "low" for MAR less than 25 mg. This same segregation corresponds to fewer than 50 samples for "very high" MAR steps, 50 to 250 samples for "high" MAR steps, 250 to 1000 samples for "moderate" MAR steps, and over 1000 samples for "low" MAR steps. This segregation and MAR designation is somewhat arbitrary and based on convenient breaks in the MAR, but it serves as a starting point for seeing how specific analytical operations and their preparation steps could fit within RLUOB constraints. Note that "very high" MAR analyses may use single samples that are above the SNM accountability threshold.

Table 2 presents a sensitivity analysis that shows the number of samples that an operational step can hold under the previous 8.4 g PE limit, the new 38.6 g PE limit, and a hypothetical 77.2 g PE limit if RLUOB is split into two separate radiological facilities.

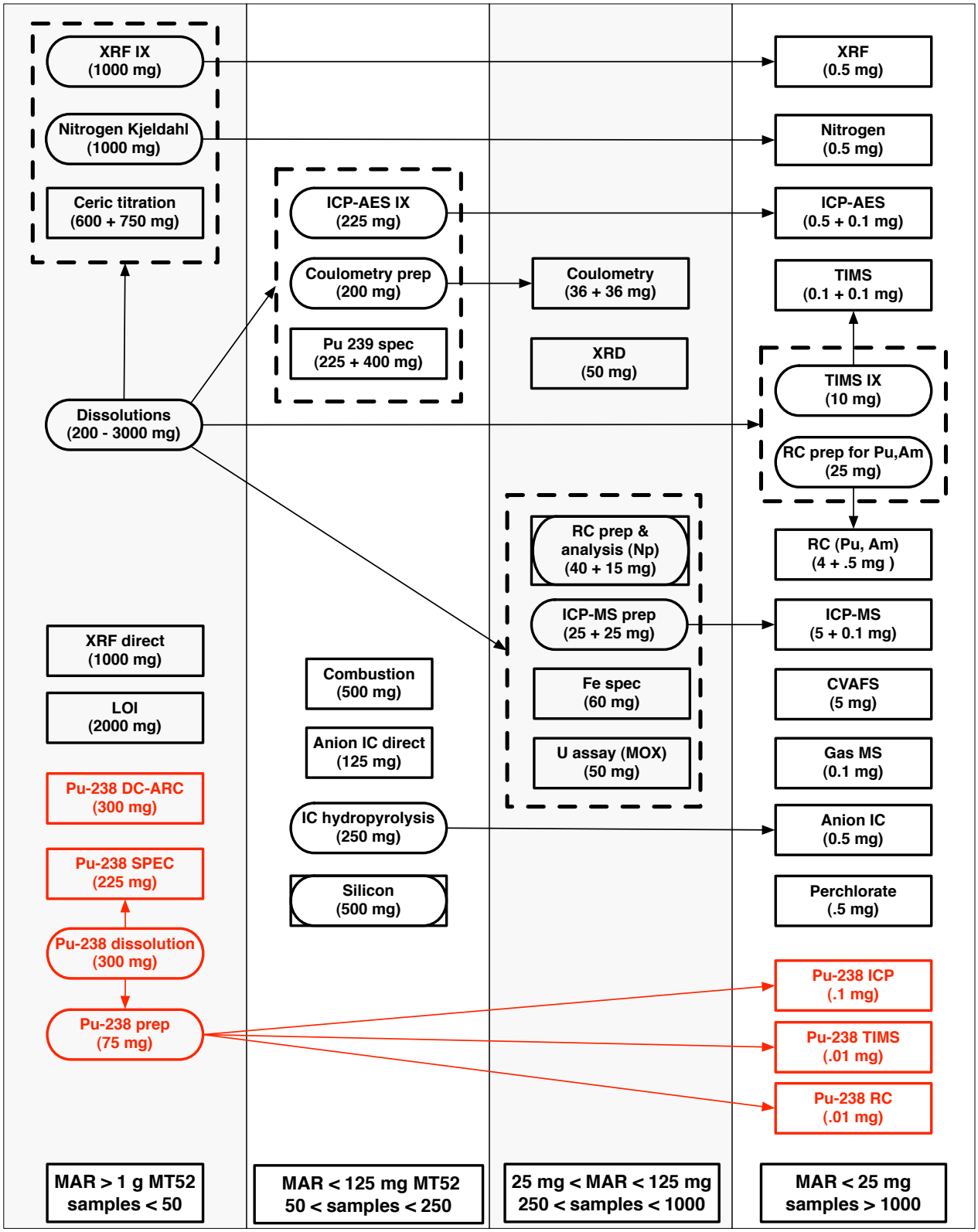

Figure 1. MAR flow map for analytical chemistry operations per sample, including standards for single analysis. Black is MT-52 samples, red is MT-83 samples. Number of samples based on 38.6 g PE MAR limit.

	# samples at 8.4 g	# samples at 38.6 g	# samples at 77.2 g
Gas MS	62687	288060	576119
TIMS	35897	164957	329915
Nitrogen	12537	57612	115224
XRF - prepped	12537	57612	115224
IC - prepped	12537	57612	115224
ICP-AES	10909	50130	100260
^{238}Pu TIMS	3784	17387	34775
^{238}Pu RC	1803	8286	16572
CVAFS	1254	5761	11522
ICP-MS	1235	5676	11353
RC (Pu, Am)	1064	4887	9774
TIMS prep	627	2881	5761
^{238}Pu ICP	394	1812	3624
RC prep (Pu/Am)	251	1152	2304
ICP-MS prep	157	721	1443
RC prep & analysis (Np)	126	577	1154
XRD	125	576	1152
U assay (MOX)	125	576	1152
Fe spec	104	478	955
coulometry	100	458	916
IC direct	50	230	461
Coulometry prep	31	144	288
Nitrogen prep	31	144	288
TIMS prep for U	31	144	288
ICP-AES prep	28	128	256
Pyrohydrolysis for IC	25	115	230
Combustion	13	58	115
^{239}Pu spec	12	55	110
XRF direct	6	29	58
XRF prep	6	29	58
Ceric titration	5	25	50
Dissolutions	3	14	29
Loss on ignition	3	14	29
^{238}Pu prep	0.53	2.43	4.86
^{238}Pu Spec	0.17	0.80	1.60
^{238}Pu dissolution	0.13	0.61	1.21
DC arc (^{238}Pu)	0.08	0.38	0.76

Table 2. Number of samples allowed for analytical chemistry operational steps under selected MAR limits.

Number of samples, requested analyses, and sample turnover rate

While there has been a great deal of variability over the years, historical data from FY2000 to 2011 indicates that an average of 500 samples and 2000 analyses per year is reasonable for planning purposes (see LA-UR-11-04600). The most commonly requested analytical techniques are radiochemistry, TIMS, ICP-AES, and ICP-MS, accounting for about two thirds of the analyses with more than a third of every sample requesting one or more of these. These are all low MAR analyses already identified as being suitable for installation in RLUOB. They all have higher MAR preparation steps.

The next grouping accounts for about a third of the analyses – interstitials (nitrogen and combustion), anions (ion chromatography and perchlorate), iron spectrophotometry, coulometry, XRF, and gas MS. These techniques are mostly in the low MAR category, with the notable exception of combustion analysis (high MAR). The remaining techniques account for less than 10% of the requested analyses.

Activity data from FY08 to FY10 was used to estimate the relative frequency of requests for specific analyses and preparation steps. This relative frequency was then used to calculate the MAR associated with running a 'typical' sample if all of the low, moderate, and high MAR activities (analyses and preps) were to be established in RLUOB. This *statistical* MAR per sample is roughly 320 mg, while the MAR if *all* the activities are requested would be 3500 mg. This order-of-magnitude difference reflects the observation that the vast majority of analytical requests are for low MAR analyses.

The rate at which samples are analyzed could be a limiting parameter for higher MAR operations at RLUOB. For example, if an analysis such as Fe spec (60 mg MT-52) takes 30 days and there are 100 requests per year, that scenerio corresponds to roughly 8 samples in process at any given time using less than 2% of the available MAR. If combustion analysis (500 mg MT-52), taking 120 days, has 100 requests per year, that corresponds to 25 samples in process using nearly 35% of the MAR (assuming 38.6 PE).

Sample preparation and staging

Samples are currently sent to CMR, where they are split into subsamples for requested analyses. Most metal and oxide samples exhibit microscopic inhomogeneity, so incoming samples and splits are often quite large to achieve high confidence in reported macroscopic composition. Capability to handle these large samples for sample preparation is currently being installed within PF-4, focusing mainly on bulk dissolution and splitting of solid and dissolved samples. Space within the PF-4 lab exists for a modest expansion of projected activities. Consolidation of most sample preparation activities within PF-4 significantly reduces the amount of material needed for the final preparation and instrumental analyses within RLUOB.

Staged MAR, whether from samples, standards, or waste, is non-productive MAR. The more analytical chemistry functions that are established within RLUOB, the greater the need to efficiently handle MAR associated with staging. Samples awaiting analysis must be staged, but readily accessible. Particularly under scenarios with a high level of centralized sample preparation, samples for specific analyses must be analyzed within a fairly short time after preparation. Standards, either solution or solid, are generally prepared in large quantity, then utilized in small quantities over their limited lifecycles. Almost all chemical analyses require the use of standards during sample analyses

and for periodic instrument calibration. An efficient operational environment mandates facile and uninterrupted access to staged standards as working stocks are depleted. Staging may be in PF-4 or inside safety-class containers in RLUOB depending on quantity, form, and facility constraints.

Material movement

Material movement is a key parameter in determining which analytical chemistry operations can be established within RLUOB, and it is likely to be *the* key parameter to operating efficiently within the facility MAR. C-AAC receives roughly 500 analytical samples per year. Movement of material, be it standards, samples, or waste, is where the parameters of MAR, sample preparation, and staging converge. The more quickly and inexpensively MAR can be moved into and out of the RLUOB facility envelope, the more efficiently analytical chemistry operations can be conducted within the limits. Even for a few hundred mg per request, 500 samples add up to hundreds of *grams* of SNM per year. Frequent material transfers into RLUOB would be needed to keep up with demand, while waste would need to leave the facility at a similar rate.

As noted in the RLUOB facility design description (TA-55-FDD-400/440, R1), "Radioactive waste must be expeditiously (re)moved in order for the RLUOB to operate as a Less-Than Hazard Category 3 Nuclear Facility." MAR from TRU waste and unexpended samples can quickly accumulate and negatively impact operations. Waste becomes *more* problematic as radiological MAR limits increase, since we now have the potential to include analytical chemistry operations that generate solid TRU as well as solutions that are too radioactive to dispose of via the industrial waste line to RLWTF.

Benefits from co-location of activities

Moving additional, higher MAR operations from CMR to RLUOB instead of waiting for CMRR to open offers the opportunity to increase operational efficiency by co-locating employee office space (RLUOB) and R&D laboratories and equipment (RLUOB) with service laboratories and equipment (RLUOB and TA-55). Consolidation of activities that share common personnel resources to a single building offers significant efficiency gains in time utilization. Consolidation of activities that share common laboratory needs and equipment offers cost savings associated with space, capital equipment, and maintenance. A busy laboratory is a healthy laboratory – a daily interaction between personnel promotes exchange of ideas, cross-training among current workers, and training for future workers.

Even consolidation of activities to two buildings within easy walking distance offers significant efficiency gains to time and personnel utilization. For operations that are not suitable for RLUOB, a certain level of convenience and efficiency would be gained by moving selected analyses to PF-4, where they would be co-located with analytical chemistry preparation activities or with the customer. Several of the current CMR ^{238}Pu analytical capabilities are slated to be installed in PF-4.

Modifications to physical configuration

RLUOB laboratory space is separated into two major areas for secure (classified) operations and for open (unclassified) activities. Analytical chemistry operations that include requests for classified analyses will have to be located within the secure space. Others may be located on either side. For safeguards and security reasons, access between the two sets of laboratory space is physically restricted, but the space was designed with some flexibility to move the security wall that separates the two areas. Adding analytical chemistry operations may require increasing the Limited/Cleared

space and possibly displacing other intended users. Depending on the operational requirements, added operations may also require other facility modifications such as enclosures, fume hoods, or utilities. The RLUOB facility design description (TA-55-FDD-400/440, R1) provides a comprehensive description of the current projections for laboratory space utilization.

RECOMMENDED PATH FORWARD

Remainder of Analytical Chemistry MAR Flow Mapping

This preliminary report has captured the major steps of key analytical chemistry operations to help determine which operational steps *could be* established in a radiological facility based on the MAR limits of Supplemental Directive NA-1 SD 1027. The operational steps are, at this point, low-resolution blocks that will be refined with respect to material input and output, equipment and personnel needs, waste forms generated, and material hold or transfer constraints. While this refinement can be made at a 'generic' level, it is most effectively accomplished based on reasonable assumptions of where specific operational steps will occur. Thus, the following two additional activities – assessments of potential locations and of material movement – are presented for consideration.

Additional Activities

Distribution and location of analytical chemistry activities

Based on the MAR flow map and sensitivity analyses, we have developed a potential distribution of analytical chemistry activities (preparation and analyses) between TA-55 and RLUOB under the new material-at-risk limit of 38.6 g PE. This proposed distribution will require considerable refinement to determine appropriate locations for each activity based on their functional and operational requirements. It will also require modifications to current practices to allow for consolidation of analytical activities and transportation of samples to a separate facility. We fully expect that this distribution of activities will change somewhat upon more extensive analysis of RLUOB and PF-4 constraints and availability.

The distribution of analytical chemistry activities presented in Figure 2 locates all of the very high and almost all high MAR activities in PF-4 with the moderate and low MAR activities in RLUOB. It also leverages facility modifications in PF-4 that are either completed, in progress, or planned in the near future. It consolidates preparation activities that have similar environmental and operational needs, such as dissolution, ion-exchange chromatography, and dilution. Outlier activities include the pyrohydrolysis for anion chromatography, and the 'dry' operations of LOI, combustion analyses, and solid-sample XRF. Where possible, final sample preparation activities are co-located with analysis equipment. The most notable exception to this co-location is the preparation of ^{238}Pu samples for TIMS and plasma spectroscopy. Some analyses, such as combustion analyses and XRD, are shown in both locations, either because equipment is already installed in PF-4 or they could potentially operate at RLUOB if material movement is agile enough.

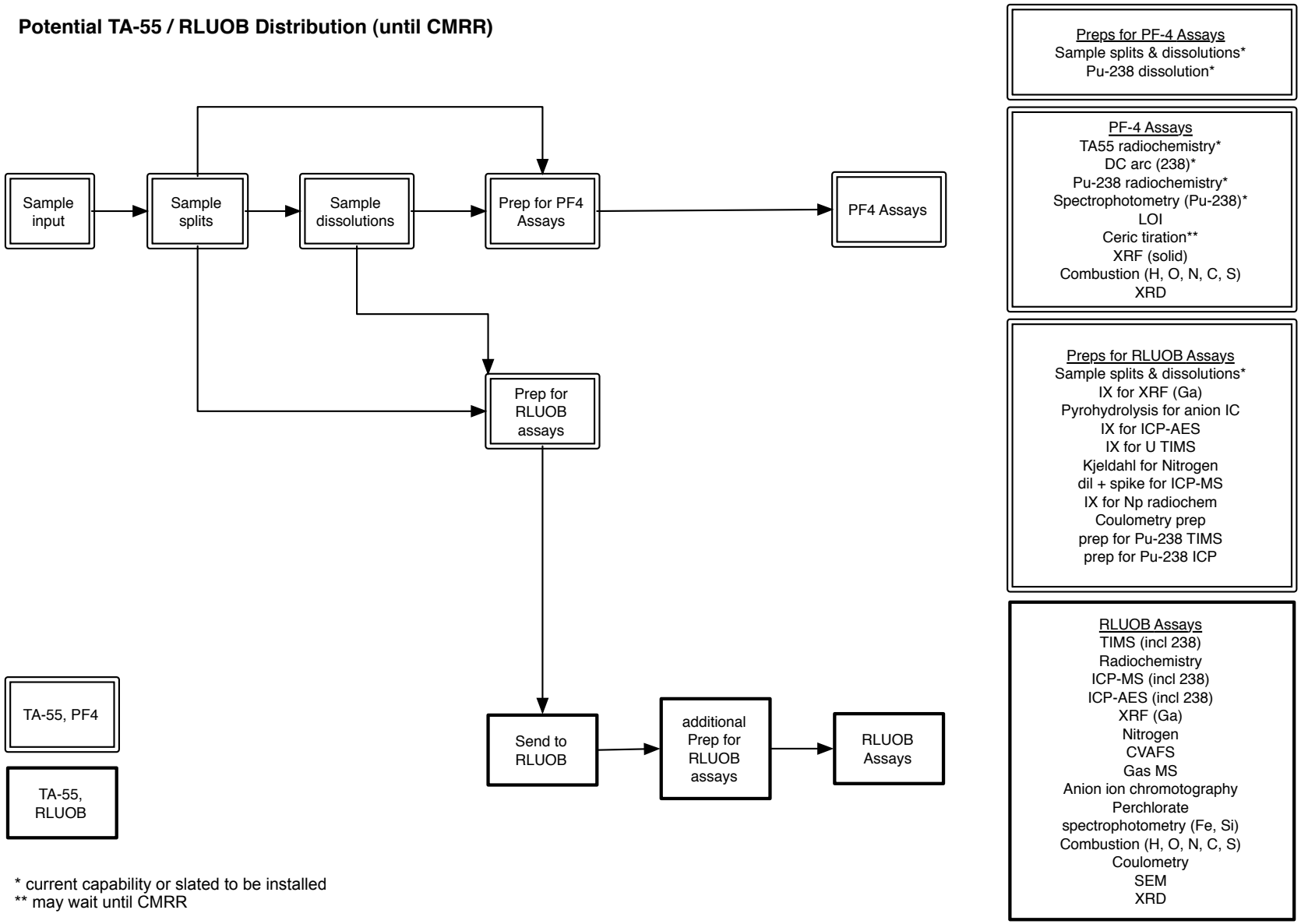

Figure 2. Potential distribution of analytical chemistry operations and preparations steps

MAR and MAR movement

Operational efficiency and cost efficiency for RLUOB are balanced under a scenario in which MAR for analysis 'trickles in' to the facility, and MAR from waste 'pulses out' of the facility. Even with the new radiological MAR limits, facile movement of material into and out of RLUOB is critical to successful and efficient operations. It is so important that not only primary methods must be identified and approved, but contingency plans for alternative methods should also be identified with approvals in place should the primary methods fail to deliver.

Transfer of samples from PF-4 to CMR currently uses the Operations Support – Packaging & Transportation group for periodic shipments. Material shipments must follow very strict protocols, including operator training, packaging, and communications. These protocols are driven by the characteristics of the consignment – accountable SNM quantities, lack of approved DOT containers, and transportation by motorized vehicle on roads. These material shipments require coordination between many people and organizations – NPI-1 to package and arrange shipment, OS-PT to conduct shipping (including rolling or static road closures), CMR-OPS to receive the shipment, and C-AAC to unpack and handle the consignment. At all points, RCTs must check containers and SNM accountability must be updated promptly. If (and when) any of these participants are unavailable, the shipment cannot occur as scheduled. Thus, shipment of large accountable samples between sites is very expensive, complicated, and time-consuming, and is often delayed due to issues with personnel or equipment resources.

With the bulk of sample preparation activities occurring in PF-4, samples being transferred to RLUOB for analysis will exhibit none of the characteristics that drive the extensive shipping process described above. The expected consignment quantities will fall between the small or limited quantity exemption (49 CFR 173.421 & .425) and accountable amounts of material (500 mg PE), thus may be hand-carried. OS-PT has shown a willingness to work with organizations to develop acceptable hand-carry and vehicle transportation protocols for specific sample types. While these sample MAR and chemical forms present some challenges, the close proximity of RLUOB to TA-55 is a distinct asset. Direct tunnel access between these facilities is being investigated as an interim measure until CMRR is constructed. Other, less expensive, options such as a formal corridor through the open space, are also possible with some modifications to established protocols.

As readily as MAR needs to flow into RLUOB, it is equally important that MAR be removed when needed. While administrative issues affect movement of MAR into RLUOB, cost issues will affect movement of MAR out of RLUOB. TRU waste costs $5000 - $6000 per drum regardless of the quantity of TRU material within. Thus, it is most cost efficient to load the waste drums as high as possible within the facility constraints. Doing so, however, adversely impacts the MAR available for active work, and greatly increases the potential for gridlock should removal of waste be delayed for some reason. Although there are no plans to do so, designation of the RLUOB waste area as a separate radiological facility from the laboratory space would substantially reduce, but not eliminate, these risks to programmatic work. Alternatives to conventional TRU waste handling must be investigated. Some of out-of-the-box approaches include returning waste solutions or solids to TA-55 for packaging in drums or removal of TRU waste from RLUOB to TA-50 for treatment and/or packaging. As with sample transfer into RLUOB, waste transfer out may be aided by the close proximity of these facilities.